Effect of particle size of limestone on Ca, Mg and K contents in soil and in sward plants

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ABSTRACT: Liming increases crop production through improved soil conditions in acidic soils. Among the effects of liming, increased availabilities of alkaline and alkaline-earth cations are worth mention. These availabilities may be affected by the particle size of applied limestone, which influences lime reactivity. The effects of particle size and application schedule of magnesium limestone were investigated on extractable Ca, Mg and K in soil, their concentrations in sward plants and dry-matter yield. Magnesium limestone of various particle sizes was applied to experimental plots at a rate of 3 t ha^{-1}, a grass-clover sward was sown, and the plots were monitored during three years. The finest limestone (< 0.25 mm) in a single application yielded the highest soil Ca and Mg concentrations extracted by Mehlich-3 and NH_4Cl. The same limestone split in three annual doses was less effective. Plots treated with the coarsest limestone (2-4 mm) did not differ from control plots. Liming had no effect on potassium, either in soil or plants. Soil concentrations of Ca, Mg and K extracted by Mehlich-3 and NH_4Cl were correlated with each other (r = 0.76, 0.75 and 0.67, respectively). NH_4Cl extracted more Ca than Mehlich-3, while the latter extracted more Mg and K than NH_4Cl. Soil Ca, Mg and K extracted by NH_4Cl were also correlated to water extractions. Mg concentration in plants correlated to soil Mg extracted by NH_4Cl or by water. Neither the concentrations nor the total contents of Ca and K in plants correlated with extractable soil Ca and K. The total dry matter yield was not affected by liming. The yield of sown species was higher in plots treated with the finest limestone than in plots limed with the coarsest limestone. Cations extracted by water or NH_4Cl explained the variance of dry matter yield.
Key words: Spain, liming, macronutrients availability, pasture yield

Efeito do tamanho das partículas de calcário nos teores de Ca, Mg e K no solo e em plantas forrageiras

RESUMO: A aplicação de calcário em solos ácidos promove aumento da produção agrícola por meio da melhoria das condições do solo. Entre os efeitos da calagem, o aumento da disponibilidade de cátions alcalinos e alcalino-terrosos são dignos de menção. Essas disponibilidades podem ser afetadas pelo tamanho das partículas do calcário aplicado, que influencia a solubilidade do mesmo. Investigaram-se os efeitos da granulometria e épocas de aplicação de calcário magnesiano nos cátions trocáveis Ca, Mg e K extraidos no solo, nas suas concentrações em plantas crescidas cultivadas nesse solo e no rendimento das suas matérias secas. Vários tamanhos de partículas de calcário magnesiano foram aplicadas às parcelas experimentais, a uma taxa de 3 t ha^{-1}, gramíneas e trevo foram plantados e as parcelas foram monitoradas durante três anos. O calcário mais fino (< 0,25 mm) em uma única aplicação proporcionou os maiores teores de Ca e Mg extraídos por Mehlich-3 e por NH_4Cl. Este mesmo calcário quando aplicado parcelado em três doses anuais foi menos eficaz. Parcelas tratadas com o clacário mais grosseiro (2-4 mm) não diferiram da testemunha. A calagem não teve efeito sobre o potássio, quer seja no solo ou nas plantas. As concentrações no solo de Ca, Mg e K extraídos por Mehlich-3 e NH_4Cl foram positivamente correlacionadas. O NH_4Cl extraiu mais Ca do que o Mehlich-3, enquanto o segundo extraíu mais Mg e K do que o NH_4Cl. O Ca, Mg e K extraídos pelo NH_4Cl foram também correlacionados com extrações por água. Concentrações de Mg em plantas estão relacionadas com concentrações de Mg no solo extraídos pelo NH_4Cl ou pela água. Nem as concentrações ou teores totais de Ca e K nas plantas correlacionaram-se com as concentrações extraídas de Ca e K do solo. O rendimento de matéria seca total não foi afetado pela calagem. A produtividade das espécies cultivadas foi maior nas parcelas tratadas com os calcários mais finos do que em parcelas com calcário mais grosseiro. Cátions extraídos pela água ou NH_4Cl correlacionaram-se com a variação da produção de matéria seca.
Palavras-chave: Espanha, calagem, disponibilidade de macronutrientes, rendimento de forrageiras

Introduction

The natural acidity of Galician soils (Spain) is mainly due to abundant precipitation and often to an acid parent material. Liming materials are commonly applied to reduce the acidity and to increase production in these soils. The particle size of the liming material is of major importance: finer materials dissolve and react more

rapidly, but their production consumes more energy, are more difficult to apply and their effects may be shorter lived. Coarser liming material acts more slowly, but its effects may persist over many years.

Scott et al. (1992) investigated the most effective particle size (between 0.005 and 3 mm) of liming material in an acid soil in Australia and concluded that the finest limestone particles produced greatest increases of pH, exchangeable Ca and wheat (*Triticum aestivum* L.) production. Haby and Leonard (2002) also observed greatest effectiveness of the finest limestone in Texas soils within the first year of trial, but at the end of three years yields were similar for the finest and coarsest limestones. Mello et al. (2003) observed a longer lasting effect of coarser limestone applied to Brazilian soils.

Different extracting solutions are currently used to evaluate the nutritional status of soils. NH_4Cl is commonly used to extract exchangeable cations, particularly in Galician soils. The Mehlich-3 extractant (Mehlich, 1984) extracts simultaneously available macro and micronutrients. Monterroso et al. (1999) reported similar and highly correlated amounts of Ca, Mg and K extracted by Mehlich-3 extractant and 1 M NH_4Cl from Galician mine soils.

The objectives of the present study were: (i) to determine the particle size of magnesium limestone that is most effective at increasing Ca, Mg and K in soil and plants; (ii) to compare Mehlich-3 extractant, 1M NH_4Cl and water as extracting agents for these elements; (iii) to relate soil extractable Ca, Mg and K to their concentrations in plants; and (iv) to elucidate which extractant is most suitable to explain the sward dry mater yield, both total and of sown species.

Material and Methods

The study was carried out in an acid soil in Galicia (NW Spain) over a 3-year period (October 1995-October 1998) in a rotation prairie/corn, in which the prairie was grown in the first two years and the corn in the last one. In this paper, we present and discuss 3-year data for soil parameters and 2-year data for plant. The soil parent material is a quaternary sediment, the land was previously a scrubland, and the soil is classified as a Haplic Umbrisol (FAO, 1998). The experimental plots were located in Castro Riberas de Lea, Lugo, Spain (43º09'37" N, 7º29'31" O). The soil texture was sandy loam (760 g kg^{-1} of sand, 117 g kg^{-1} of silt and 123 g kg^{-1} of clay); the pH in water was 4.85 and pH in KCl was 4.23 (soil:solution 1:2.5); exchangeable Ca, Mg, Na, K and Al were 32.7, 24.0, 0.5, 1.3 and 37.4 $mmol_c$ kg^{-1}, respectively; effective CEC was 74.3 $mmol_c$ kg^{-1} and Al saturation was 50%.

According to the bioclimatic classification of Papadakis (1966) the zone belongs to the cool temperate Mediterranean climatic unit, and according to Allué (1966) it is a subhumid Mediterranean phytoclimatic subregion with Central European tendencies. The mean monthly temperature in the period of study ranged between 6.6 and 18.1ºC (mean 11.2ºC) in 1996, between 5.4 and 18.7ºC (mean 12.8ºC) in 1997, and between 5.8 and 19.8ºC (mean 12.2ºC) in 1998. The total rainfall was 1019 mm in 1996, 1098 mm in 1997 and 942 mm in 1998.

Magnesium limestone (3 t ha^{-1}) was applied to 24 experimental plots, 5 × 4 m^2 each. The chemical composition of the limestone was 87.8% of $CaCO_3$ equivalent, 254 g kg^{-1} of Ca, 69 g kg^{-1} of Mg and 0.16 g kg^{-1} of K). Before application, the limestone was crushed and separated into different fractions by passing through various sieves, to obtain the materials for the treatments: 2-4 mm (treatment 4), 0.5-2 mm (treatment 2), 0.25-0.5 mm (treatment 0.5) and < 0.25 mm (treatments 0.25 and 0.25f). Limestone was applied as a single dose of 3 t ha^{-1} at sowing (October 1995), except in treatment 0.25f, where three separate doses of 1 t ha^{-1} were applied in October 1995, 1996 and 1997 (to provide a final amount of 3 t ha^{-1}). The soil was tilled by a rotary cultivator, then lime and fertilizers were applied by hand and incorporated into the topsoil by the rotary cultivation. Each treatment was replicated four times, and four control plots (no lime) were sown at the same time. A randomized experimental design was used. NPK fertilizer (8:24:16) was added to all 24 plots (500 kg ha^{-1}) at sowing and in May and October 1996, 1997 and 1998. Phosphorus was in the form of calcium phosphate. *Lolium multiflorum* Lam. (Italian ryegrass), *Dactylis glomerata* L. (cocksfoot), *Trifolium repens* L. (white clover) and *Trifolium pratense* L. (red clover), at rates of 15, 5, 2 and 8 kg ha^{-1}, respectively, were broadcast sown in October 1995, after the second rotary cultivation.

Soil samples (0-20 cm) were collected in autumn, winter, spring and summer, during the three years of study for general analyses (data not shown). Ten individual samples were collected from each experimental plot and bulked into a composite sample. Samples were air-dried and sieved (< 2 mm) prior to analysis. Samples from April and July were used to compare the extracting capacity of the three extractants under study. Calcium, magnesium and potassium were extracted by 1 M NH_4Cl (Peech et al., 1947), Mehlich-3 extractant (Mehlich, 1984) and water (1:10 soil:water ratio) and determined by atomic absorption (Ca and Mg) or atomic emission (K) spectrophotometry.

Samples of plant species were collected in July and October 1996 and 1997, at harvest. To this purpose, an area of 10 (2 × 5) m^2 was cut; the plant material from each plot was homogenized and a 1-kg fresh-weight sample obtained and reserved for analysis. Samples were oven-dried at 105ºC until constant weight to determine dry matter yield. In another sub-sample, the species were separated and dried to determine the yield for each species. Powdered samples were digested by concentrated H_2SO_4 and H_2O_2 (Jones et al., 1991), and Ca, Mg and K in the digests were determined by atomic absorption (Ca, Mg) or emission (K) spectrophotometry. Phosphorus was determined in digests by visible spectrophotometry. Results of yield and plant analyses are presented and discussed only for summer cuts, because yield was very low in autumn cuts.

Data were subjected to three-way analysis of variance, being treatment, date and plant species the factors analysed, and linear regression analysis, using the statistical programme SPSS, version SPSS 12.0 for Windows.

Results and Discussion

The Ca concentrations in both Mehlich-3 and NH_4Cl extracts presented a trend to higher values in plots limed with finer limestone. Differences were observed only in Mehlich-3 Ca in spring of the first and last years of trial (Table 1). The lowest values generally corresponded to the plots treated with the coarsest limestone (treatments 2 and 4), which did not differ from those obtained for the control plots. The finer limestone (treatments 0.25 and 0.5) was more effective, as it dissolved and acted more quickly compared to coarser limestone and, moreover, maintained the highest levels

Table 1 – Ca, Mg and K extracted from soil by extractants.

		Ca			Mg			K		
		Mehlich-3	1M NH_4Cl	Water	Mehlich-3	1M NH_4Cl	Water	Mehlich-3	1M NH_4Cl	Water
		mg kg^{-1}								
April 96	Control	317^{ab}	1580	38.2	110^{b}	36.0^{d}	2.1^{c}	124	69.2	32.0
	4	275^{ab}	1540	39.1	116^{b}	60.0^{cd}	3.2^{c}	115	67.3	30.1
	2	246^{b}	1340	45.3	134^{b}	120.0^{bc}	6.1^{b}	99	63.3	25.1
	0.5	413^{ab}	1620	44.2	218^{a}	180.2^{ab}	9.0^{a}	111	75.1	28.2
	0.25f	310^{ab}	1480	36.2	132^{b}	120.1^{abc}	4.2^{c}	107	69.2	35.1
	0.25	442^{a}	1780	53.0	210^{ab}	192.0^{a}	10.1^{a}	123	63.4	25.0
July 96	Control	286	1320	32.1	66^{d}	12.3^{c}	1.4^{d}	152	160.9	41.0^{a}
	4	303	1360	30.2	95^{cd}	24.2^{c}	3.1^{d}	142	144.3	39.1^{a}
	2	370	1380	33.0	167^{bc}	84.1^{b}	7.1^{bc}	147	154.0	41.2^{ab}
	0.5	405	1460	33.1	255^{a}	144.0^{a}	9.3^{ab}	169	156	41.3^{ab}
	0.25f	363	1440	33.2	145^{bcd}	48.1^{bc}	5.1^{cd}	135	167.7	36.1^{b}
	0.25	405	1680	43.3	187^{ab}	168.0^{a}	11.0^{a}	145	193.1	43.1^{a}
April 97	Control	322	1220	76.0	39^{b}	24.1^{b}	4.1^{b}	192	213.2	84.0
	4	215	1360	91.2	59^{b}	60.2^{b}	8.2^{ab}	150	194.0	81.0
	2	261	1260	81.1	114^{b}	132.3^{a}	17.3^{b}	158	186.2	56.0
	0.5	317	1680	55.1	209^{a}	180.0^{a}	16.0^{a}	161	199.9	47.1
	0.25f	397	1520	56.2	126^{ab}	156.1^{a}	8.1^{ab}	161	187.2	38.1
	0.25	489	1900	69.3	210^{a}	204.2^{a}	17.0^{a}	186	205.7	53.2
July 97	Control	221	1440	158.2	35^{c}	24.1^{d}	7.0^{c}	158	195.9	70.0
	4	231	1540	132.1	73^{bc}	72.1^{cd}	17.1^{bc}	138	186.2	68.1
	2	342	1600	125.3	178^{ab}	168.0^{ab}	36.1^{ab}	180	195.0	63.3
	0.5	371	1780	150.0	215^{a}	192.0^{ab}	46.3^{a}	191	204.7	69.3
	0.25f	356	1720	161.0	132^{abc}	156.3^{bc}	37.0^{ab}	186	202.8	63.2
	0.25	468	1980	150.1	207^{a}	192.2^{a}	44.0^{a}	157	198.9	60.2
April 98	Control	169^{c}	1300	18.2	40^{b}	48.0^{c}	1.1^{c}	133	127.7	32.0
	4	160^{c}	1300	34.1	58^{b}	96.0^{b}	5.0^{b}	121	141.4	40.2
	2	227^{bc}	1360	23.3	155^{ab}	192.2^{a}	6.2^{a}	126	105.3	25.3
	0.5	206^{bc}	1420	34.1	142^{ab}	204.1^{a}	8.3^{a}	130	122.8	33.2
	0.25f	440^{a}	1480	26.2	236^{a}	192.0^{a}	5.1^{a}	148	144.3	31.1
	0.25	394^{ab}	1660	29.3	196^{a}	204.0^{a}	6.4^{a}	125	120.9	30.0
July 98	Control	249	1380	101.0	76^{c}	36.2^{c}	5.0^{a}	212	168.7	83.1
	4	328	1400	96.1	160^{bc}	144.0^{ab}	11.1^{ab}	191	178.4	78.1
	2	312	1340	91.3	201^{ab}	192.0^{ab}	15.1^{ab}	177	140.4	73.0
	0.5	336	1380	111.2	229^{ab}	192.1^{ab}	21.1^{ab}	214	178.4	79.2
	0.25^{f}	416	1520	98.1	268^{a}	204.1^{a}	19.2^{b}	217	205.7	72.2
	0.25	534	1820	109.0	251^{ab}	204.2^{a}	20.0^{b}	211	174.5	66.3

Control: no limestone; 4: diameter of limestone particles between 2 and 4 mm; 2: diameter of limestone particles between 0.5 and 2 mm; 0.5: diameter of limestone particles between 0.25 and 0.5 mm; 0.25: diameter of limestone particles < 0.25 mm; 0.25f: limestone less than 0.25 mm in diameter applied in 3 separate doses. Different letters indicate differences ($p < 0.05$) between treatments.

of Ca during the three years of study. Even at the end of the three-year trial there were differences ($p < 0.05$) in Ca concentrations between plots treated with limestone < 0.25 mm and control plots (Table 1). Conversely, the coarsest limestone (0.5-2 mm and 2-4 mm) hardly modified the Ca concentrations relative to control plots; the coarse particle size appears to hinder the incorporation of the material into the soil.

Scott et al. (1992) reported that the effect of coarse limestone (3 mm) on exchangeable Ca became apparent only three years after application, which indicates the slow release of Ca from coarse limestone, whereas in a field trial with fine limestone (< 0.25 mm) Fernández-Sanjurjo et al. (1995) observed a residual effect of liming 7 years after application. On the other hand, the differences in concentrations of Mehlich-3 and NH_4Cl extractable Ca between treatments 0.25 (3 t ha^{-1} limestone of < 0.25 mm diameter in a single application) and 0.25f (1 t ha^{-1} limestone of < 0.25 mm diameter every year for three years) indicate the greater efficacy of the former treatment (Table 1). In treatment 0.25f, even when the entire limestone dosage (3 t ha^{-1}) was completed, the concentration of Ca extracted by 1M NH_4Cl was lower than in plots to which the same limestone was applied as a single dose.

The concentrations of water-soluble Ca do not differ among treatments (Table 1). The higher concentrations obtained in July than in April (excepting the first year) in all plots may be due to the NPK fertilisation applied in May every year, and also to the low rainfall in this period, which would result in low leaching losses. The calcium phosphate in the fertilizer may have increased the amounts of soluble Ca in soil; in addition, the K supplied with the fertilizer may displace Ca from the exchange sites, thereby increasing its concentration in solution. In fact, there was a significant, although low, correlation between exchangeable K and soluble Ca ($r = 0.39$, $p < 0.01$).

A close correlation was observed between Ca extracted by the Mehlich-3 extractant and that extracted by NH_4Cl ($r = 0.77$, $p < 0.01$), although NH_4Cl extracted three to eight times as much Ca as Mehlich-3 extractant (Figure 1). These data differ from those obtained by Monterroso et al. (1999) for mine soils, according to which in most samples both extractants extracted similar quantities of Ca; yet in some samples, rich in Ca and Mg carbonates, the Mehlich-3 extractant extracted two to three times as much Ca as NH_4Cl. In studies carried out to compare the Ca extracted by ammonium acetate and Mehlich-3, some authors found that the latter reagent extracted greater amounts (Mehlich, 1984; Gartley et al., 2002) and others reported that both reagents extracted similar amounts (Wendt, 1995).

In the present study, the lower extraction of Ca by the Mehlich-3 extractant may be explained by the presence of NH_4F in Mehlich-3 extractant, which may result in precipitation of CaF_2 in samples from limed plots. A similar situation was observed by Gago et al. (2002) in Galician pasture soils unlike forest soils. Therefore,

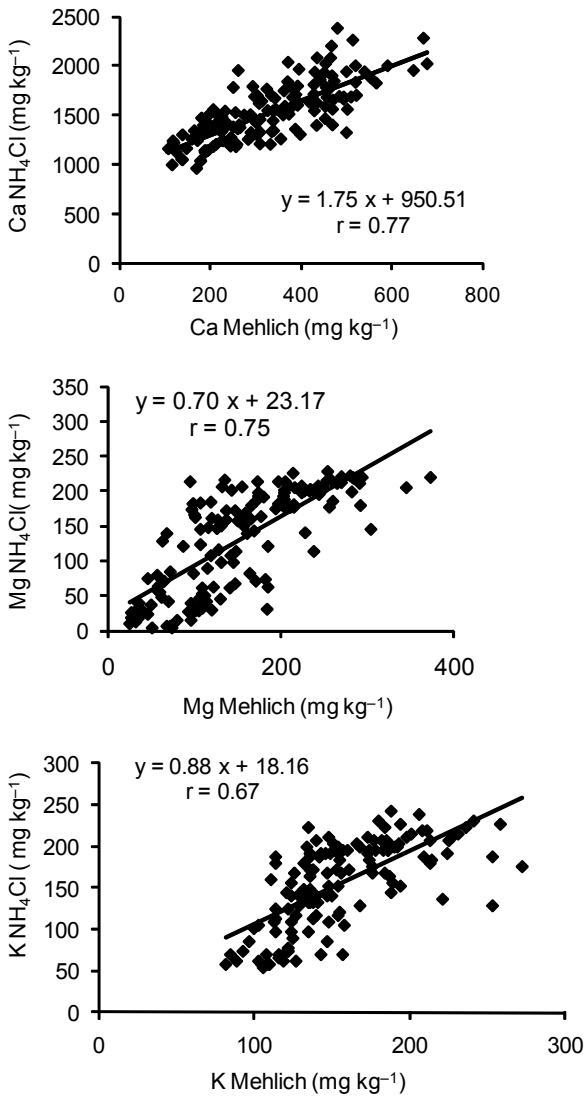

Figure 1 – Correlations between extractions of Ca, Mg and K by Mehlich-3 and 1 M NH_4Cl ($p < 0.01$).

the Mehlich-3 extractant may underestimate the available Ca in limed soils. As expected, the water extracted much less calcium than ammonium chloride or Mehlich-3 extractant. The water-soluble Ca was correlated with the water-soluble Mg ($r = 0.78$, $p < 0.01$) and water-soluble K ($r = 0.49$, $p < 0.01$).

The lack of differences in Ca concentration in plants between limed and unlimed plots was quite unexpected (Figure 2) but coincides with findings by other authors (Fystro and Bakken, 2005). Often, the application of any nutrient increases its concentration in plants (Whitehead, 1966). However, in some cases, the supply of a nutrient may increase plant growth without increasing the concentration of the nutrient itself, as a consequence of a dilution effect (Reid and Horvath, 1980). The latter authors reported that the application of a severely deficient nutrient increases growth and mineral uptake, but not necessarily the nutrient concentration in the plant. With

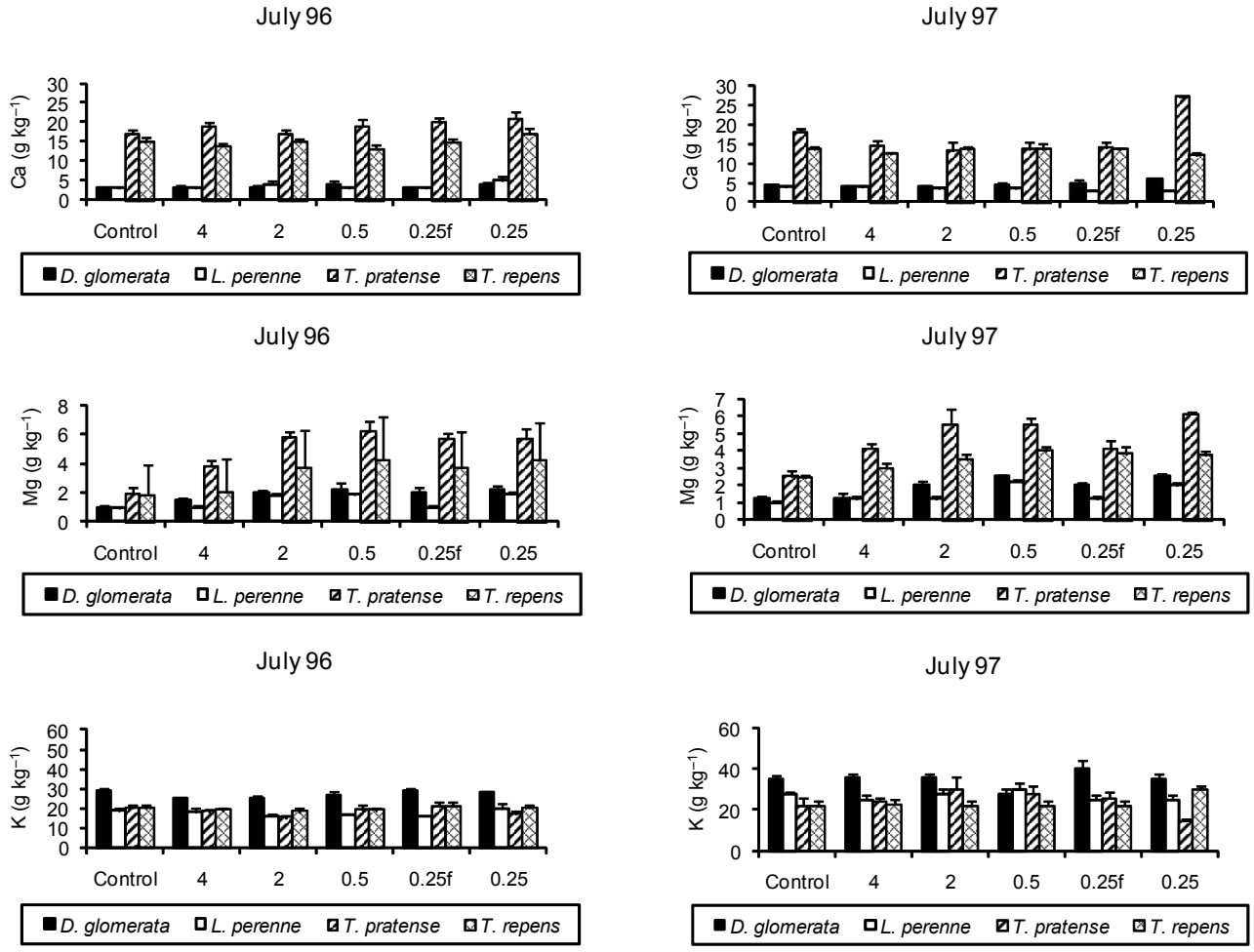

Figure 2 – Concentrations of Ca, Mg and K in the sown species for each treatment in summer harvests. (Control: no limestone; 4: diameter of limestone particles between 2 and 4 mm; 2: diameter of limestone particles between 0.5 and 2 mm; 0.5: diameter of limestone particles between 0.25 and 0.5 mm; 0.25: diameter of limestone particles < 0.25 mm; 0.25f: limestone less than 0.25 mm in diameter applied in 3 separate doses). The vertical bars represent the standard errors.

a higher nutrient supply, its concentration in plant will increase, with or without a yield increase.

As for plant species, clovers had higher ($p < 0.01$) calcium concentrations than grasses (Figure 2). These results agree with those reported by other authors (Whitehead, 1995). Analysis of the Ca extraction by plants (the value of the Ca concentration multiplied by the plant dry-weight yield) in the four plant species, for each treatment in the two summer harvests, showed that in July 1996 the extractions were highest in the ryegrass and the two legume species (*T. repens* and *T. pratense*) growing in the plots treated with the finest limestone (< 0.25 mm), whereas, the plants growing in plots treated with the other particle-sized limestone did not differ from the control (Figure 3). At the second harvest (July 1997) the highest plant Ca extractions corresponded to the ryegrass, cocksfoot and red clover growing in the plots treated with the finest limestone. The treatments with limestone > 0.25 mm did not differ from control for any date or species.

There were no correlations between either the concentrations in plant or the Ca extraction and the concentration of soil Ca extracted by any of the reagents tested. Thus the Ca uptake did not appear to depend on its concentration in soil, but rather on the interaction between this nutrient and others such as K, Mg and P (Kovacevic et al., 2004). In this respect, negative correlations ($p < 0.01$) were observed in legumes between plant concentrations of Ca and K (r = -0.70 in red clover).

The control plots presented the Mg modifier as defined by Buol et al. (1975); Mg extracted by 1 M NH_4Cl lower than 48 mg kg^{-1}) during the entire period of study (Table 1). This limiting factor was also observed in the first year of study in plots treated with the coarsest limestone (2 to 4 mm). In general, throughout the study period, the lowest concentrations of extractable Mg were obtained in the control plots and in those limed with the coarsest limestone (Table 1). Lower Mg concentrations were measured in the plots treated with the finest limestone in split application (0.25f) than in the plots treated with the same limestone in a single application.

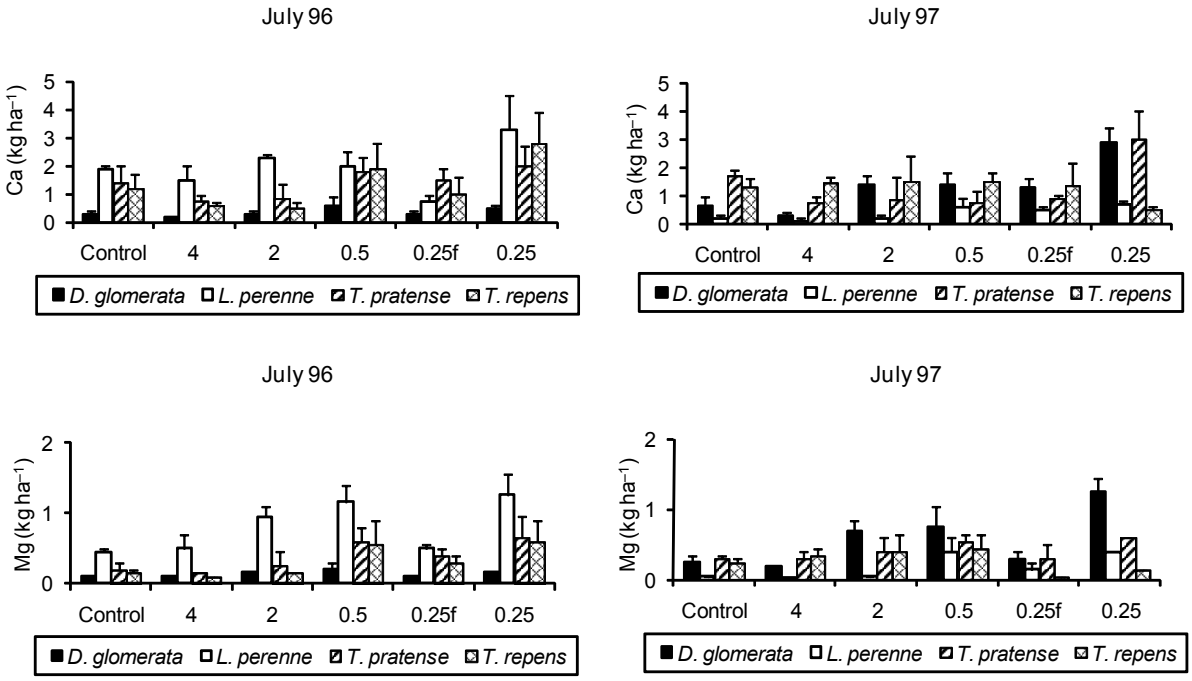

Figure 3 – Ca and Mg extraction by pasture species in summer harvests. Treatments as in Figure 2. Vertical bars represent the standard errors.

Several authors have reported a considerable reduction of exchangeable Mg after application of $CaCO_3$, because of the displacement of Mg by Ca in the exchange complex (Santano and Espejo, 1997). This is why the use of dolomitic limestone is recommended to prevent Mg deficiencies (Riggs et al., 1995). In the present study, the use of dolomitic limestone, excepting the coarsest one, resulted in higher concentrations of Mg than in the control plots. These results are consistent with those of other authors (Ernani et al., 1998; Dugalic et al., 2008; Araújo et al., 2009), who indicate that this amending agent increases the retention of Mg due to the increase of effective cation exchange capacity (resulting from the pH increase) and to an altered Ca/Mg ratio. As occurred with Ca, the highest concentrations of water-soluble Mg (excepting the first year) were obtained in July in all plots, again probably due to the application of NPK fertilizer in May. The K may displace Mg from the exchange sites thereby increasing the content of the latter in the soil solution.

The Mg extracted by Mehlich-3 extractant correlated closely with that extracted by 1 M NH_4Cl ($r = 0.75$, $p < 0.01$) (Figure 1), for the entire sampling period. In general, in the first year of trial Mehlich-3 extractant extracted more Mg than 1 M NH_4Cl. However, in the following two years, the ratio of Mg extracted by the two methods was closer to 1 and in some cases more Mg was extracted by 1 M NH_4Cl than by Mehlich-3 extractant. Therefore, it appears that in the first months after the liming, part of the Mg incorporated will become bound to positions from which it cannot be extracted by 1 M NH_4Cl, in other words, part of the Mg will not be readily exchangeable. Over time, the Mg may become readily exchangeable and thus the extractive power of the two reagents becomes similar. Monterroso et al. (1999) reported correlation between the Mg extracted by both methods, with similar amounts extracted. Some authors have also reported that Mehlich-3 extractant and ammonium acetate extract similar amounts (Wendt, 1995; Gartley et al., 2002), although Mehlich (1984) obtained better extraction of Mg with the Mehlich-3 extractant. Water-soluble Mg was far less than magnesium extractable by NH_4Cl or Mehlich-3 extractant. Similarly to calcium, the water-soluble Mg correlated with that extracted by 1M NH_4Cl ($r = 0.56$, $p < 0.01$), but not with that extracted by Mehlich-3 extractant.

The Mg concentration in plant tissues was generally higher for all species in the plots treated with the finest limestone (< 0.25 or 0.25-0.5 mm) than in plants growing in plots treated with the coarsest limestone (2 to 4 mm) and control plots (Figure 2). A higher Mg concentration in forage reduces grass tetany risk (Aydin and Uzun, 2008). The differences found between treatments in terms of the plant concentration of Mg, but not of Ca, are consistent with the results obtained by Jones et al. (1991). Furthermore, Stevens and Laughlin (1996) observed an increase of Mg concentration in pasture species growing in plots limed with magnesium limestone. As for plant species, clovers had higher Mg concentrations than grasses ($p < 0.01$) (Figure 2). These results agree with those reported by other authors (Whitehead, 1995).

The concentration of Mg in plants was correlated with Mg concentrations in the NH_4Cl and aqueous soil extracts, considering the extractions for each sampling

(Table 2). Regarding the extraction of Mg by plants, the lowest values were obtained in the plants from the control plots and those treated with the coarsest lime in both summer harvests. The highest extractions generally corresponded to those plants treated with the finest limestone (0.25-0.5 mm and < 0.25 mm, Figure 3), as occurred with the concentration of Mg.

There were no differences among treatments in terms of the concentration of potassium extracted by the different methods (Table 1), undoubtedly because of the addition of NPK fertiliser to all plots. Liming was not observed to affect exchangeable K, in accordance with the findings of other studies (Peregrina et al., 2008). Until the second application of NPK in May 1996 (the first was carried out in October 1995), all the plots presented the *k* modifier as defined by Buol et al. (1975) (exchangeable K < 78 mg kg^{-1}; Table 1). The increase in exchangeable (extracted by NH_4Cl) K observed in all treatments (including control plots) after the second application of NPK may be related to the fertilizer. When a potassium salt is added to soil, the concentration of K in soil solution increases rapidly and a fraction may gradually pass to the cation exchange sites (Cherney et al., 2004) and another may be fixed as a non-exchangeable form (Mengel and Kirby, 1980). This fixed K may return to available forms in the long term.

The K extracted by the Mehlich-3 extractant and 1 M NH_4Cl correlated significantly ($r = 0.67$, $p < 0.01$) (Figure 1). The ratio of Mehlich-3-extracted K /exchangeable K ranged between 0.76 and 2.02. Therefore, as in the case of Mg, there were some samples in which Mehlich-3 extractant was more effective than 1 M NH_4Cl and others in which the opposite was true. As a general trend, the Mehlich-3 extractant was more effective at extracting K at the start and the end of the study, whereas in 1997 1M NH_4Cl was more effective. Monterroso et al. (1999) obtained similar extraction of K by both methods in mine soils. In studies comparing extraction of K by Mehlich-3 and ammonium acetate, some authors have reported extraction of similar amounts (Gartley et al., 2002), whereas others found that the Mehlich-3 extractant was more effective (Mehlich, 1984; Wendt, 1995). Like Ca and Mg, K was less effectively extracted by water than by NH_4Cl or Mehlich-3 extractant. There was also a high correlation between the K extracted by 1 M NH_4Cl and the water-soluble K ($r = 0.62$, $p < 0.01$), but not between the latter and the K extracted by Mehlich-3 extractant.

There were no differences among the treated plots or between the treated plots and the control plots in the K concentrations in plants, as found for the exchangeable and soluble K in soil (Figure 2). These results are in accordance with those obtained by other authors (Stevens and Laughlin, 1996; Brown et al., 2008). There were some differences in the K concentration among the plant species (Figure 2). Thus, at the first harvest (summer 1996) K was present at higher concentrations in *Dactylis glomerata* than in the other species; later the concentrations of K were higher in the two grass species than in the leguminous species (autumn 1996); at the last two sampling times, there were no differences in the concentrations of K among the different species.

When a soil is deficient in K the concentration of this element is higher in grass than in leguminous species, and as the levels of deficiency are rectified, the concentration of K tends to become similar in both

Table 2 – Correlations between Mg concentrations in the pasture species and concentrations of soil Mg extractable by NH_4Cl and water.

	Ryegrass	Cocksfoot	Red clover	White clover
July 1996:				
NH_4Cl Mg	0.88**	0.83**	0.75**	0.82**
water Mg	0.86**	0.84**	0.78**	0.83**
July 1997:				
NH_4Cl Mg	0.79**	0.73**	0.82**	0.78**
water Mg	0.79**	0.64**	0.83**	0.74**

**$p < 0.01$

Table 3 – Explanation of the variance of dry matter yield in each harvest.

Harvest	Parameter	Variable	R^2
July 1996	Sown and volunteer plants dry matter	Available P	0.40
		Available P, NH_4Cl K	0.52
July 1997	Sown and volunteer plants dry matter	Soluble K	0.35
		Soluble K, NH_4Cl Na	0.65
July 1997	Lolium multiflorum dry matter	NH_4Cl Ca	0.60

$p < 0.01$

(McNaught, 1958). Grass species are more competitive when K is scarce (McNaught, 1958). In the present study, the concentrations of K extracted by 1 M NH_4Cl were considered deficient (< 0.2 $cmol_{(+)}$ kg^{-1}, Buol et al., 1975) until July 1996, which may affect the concentration of K in plants in the two harvests in this year. In 1997, K was not deficient in the soil, which may explain the lack of differences between grass and leguminous species. As regards the K extraction by plants, no differences among treatments were observed. As occurred with Ca, neither the concentration in plant nor the K extraction by plant correlated with soil K extracted by any of the reagents studied.

Dry matter yield ranged between 5.5 and 6.1 t ha^{-1} yr^{-1} in the July 1996 harvest and between 3.9 and 4.4 t ha^{-1} yr^{-1} in the July 1997 harvest (Figure 4). These values were lower than the average range of 6-12 t ha^{-1} yr^{-1} reported by Mosquera and González (1999) for Northern Spain. In July 1996, no differences were observed among treatments either in total or sown-species yields, although a trend was perceived to higher yields of sown species in treatments 0.25 and 0.5 (Figure 4). In July 1997 yields of both total and sown species were somewhat higher in treatment 0.25 (Figure 4); in the case of sown species the difference is significant between treatment 0.25 and treatments 4 or control (Figure 4). We interpret the lack of differences between treatments in total forage yield as a result of volunteer species adaption to acid conditions. On the other hand, liming influences yield of sown species which are more demanding in terms of soil fertility.

A stepwise linear regression analysis was performed to correlate dry matter yields in summer harvests to several soil parameters. Different soil parameters explain the variance of various yields in both harvests (Table 3). So, for total dry matter yield, in July 1996 available P and exchangeable K explained 52% of the variance, while in July 1997 65% of the variance is explained by water-soluble K and exchangeable Na. In July 97, the exchangeable Ca (extracted by NH_4Cl 1 M) explained 60% the dry matter yield of ryegrass. Hence, Ca and K extracted by 1 M NH_4Cl or by water seem to reflect plant uptake more appropriately than cations extracted by Mehlich-3 extractant.

Conclusions

The magnesium limestone of particle size < 0.25 mm, applied as a single dose of 3 t ha^{-1}, was the most effective at providing the highest concentrations of soil extractable Ca and Mg and the highest yield of sown species. Ca, Mg and K extracted by 1M NH_4Cl correlated to the Mehlich-3 and water extractions. The Mg concentrations and extractions by plants were much more affected by liming than those of Ca, particularly for the fine limestone. Water and 1M NH_4Cl seem better predictors of plant uptake than Mehlich-3.

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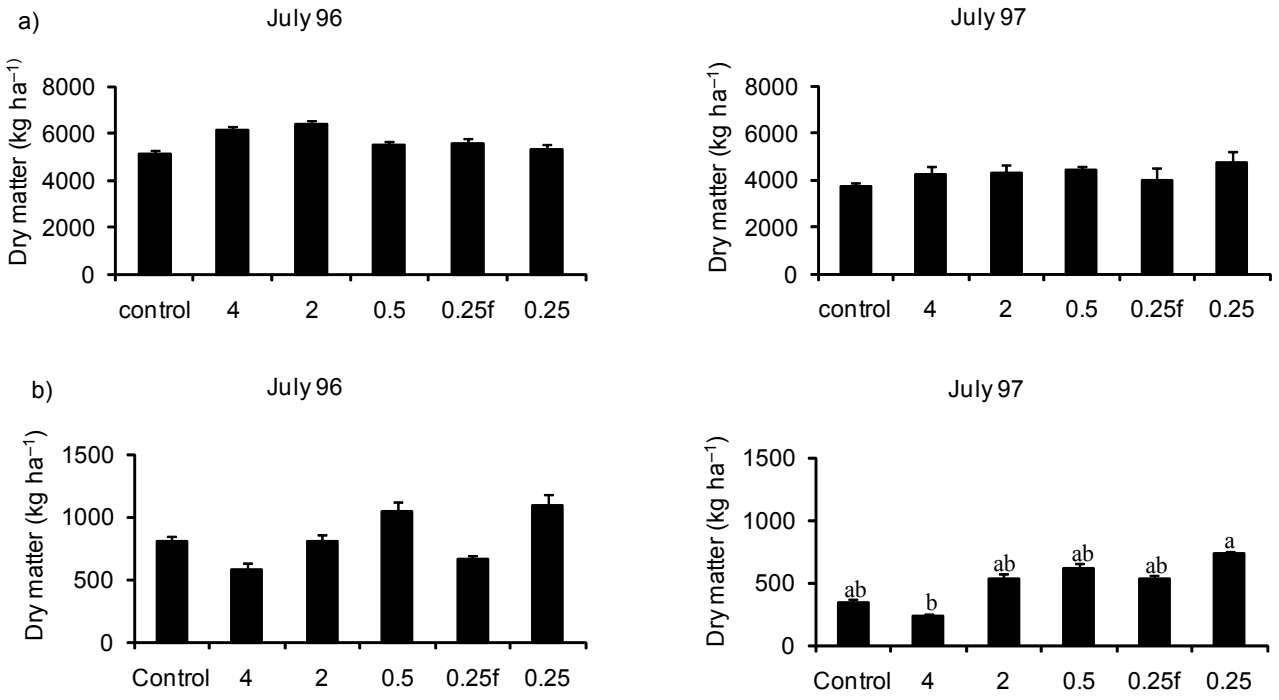

Figure 4 – a) Dry matter yield of sown and volunteer species. b) Dry matter yield of sown species. Different letters indicate differences (p < 0.05) between treatments. The vertical bars represent the standard errors.

References

Allué, J.L. 1966. Phytoclimatic Subregions of Spain. I.F.I.E. Ministerio de Agricultura, Madrid, Spain. (in Spanish).

Araújo, S.R.; Dematte, J.A.M.; Garbuio, F.J. 2009. Application of lime with different reaction degrees: chemical changes in soil under corn. Revista Brasileira de Ciência do Solo 33: 1755-1764 (in Portuguese, with abstract in English).

Aydin, I.; Uzun, F. 2008. Potential decrease of grass tetany risk in rangelands combining N and K fertilization with MgO treatments. European Journal of Agronomy 29: 33-37.

Brown, T.T. ; Koenig, R.T.; Huggins, D.R.; Harsh, J.B.; Rossi, R.E. 2008. Lime effects on soil acidity, crop yield, and aluminum chemistry in direct-seeded cropping systems. Soil Science Society of America 72: 634-640.

Buol, S.W.; Sanchez, P.Q.; Cate, R.B.; Granger, M.A. 1975. Soil fertility capability classification for fertility management. p. 126-141. In: Bornemisza E.; Alvarado, A., eds. Soil Management in Tropical America. North Carolina State University, Raleigh, NC, USA.

Cherney, J.H.; Ketterings, Q.M.; Orloski, J.L. 2004. Plant and Soil elemental status as influenced by multi-year nitrogen and potassium fertilization. Journal of Plant Nutrition. 27: 991-1014.

Dugalic, G.; Gajic, B.; Katic, S.; Stevovic, V. 2008. Influence of liming on yield and chemical composition of alfalfa on an acid soil. Cereal Research Communications 36: 995-998.

Ernani, P.R.; Nascimento, J.A.L.; Oliveira, L.C. 1998. Increase of grain and green matter of corn by liming. Revista Brasileira de Ciência do Solo 22: 275-80.

Food and Agriculture Organization of the United Nations [FAO]. 1998. World Reference Base for Soil Resources. Rome, Italy. (World Soil Resources Reports, 84).

Fernández-Sanjurjo, M.J.; Álvarez, E.; García-Rodeja, E. 1995. Effect of liming on certain properties of the soil solution, the colloidal fraction and the availability of phosphorus. Edafología 1: 19-127. (in Spanish).

Fystro, G.; Bakken, A.K. 2005. Soil reaction, yields and herbage element content as affected by lime applied on established leys in a multi-site field trial. Journal of Agricultural Science. 143: 407-420.

Gago, C.; Fernández Marcos. M.L.; Álvarez, E. 2002. Aqueous aluminium species in forest soils affected by fluoride emissions from an aluminium smelter in NW Spain. Fluoride 35: 1-12.

Gartley, K.L.; Sims, J.T.; Olsen, C.T.; Chu, P. 2002. Comparison of soil test extractants used in Mid-Atlantic United States. Communications in Soil Science and Plant Analysis. 33: 873-895.

Haby, V.A; Leonard, A.T. 2002. Limestone quality and effectiveness for neutralizing soil acidity. Communications in Soil Science and Plant Analysis. 33: 2935-2948.

Jones, J.B.; Wolf, B.; Mills, H.A. 1991. Plant Analysis Handbook: A Practical Sampling, Preparation, Analysis, and Interpreting Guide. Micro-Macro Publishing, Georgia, GA, USA.

Kovacevic, V.; Banaj, D.; Antunovic, M.; Petosic, D. 2004. Fertilization impacts on the yield and nutritional status of maize (*Zea mays* L.). Cereal Research Communications 32: 403-410.

McNaught, K.J. 1958. Potassium deficiency in pastures. I. Potassium content of legumes and grasses. New Zealand Journal of Agricultural Research 1: 148-181.

Mehlich, A. 1984. Mehlich-3 soil test extractant: a modification of Mehlich 2 extractant. Communications in Soil Science and Plant Analysis 15: 1409-1416.

Mello, J.C.A.; Boas, R.L.V.; Lima, E.V.; Crusciol, C.A.C.; Bull, L.T. 2003. Changes of chemical soil characteristics due to doses and particle sizes of limestone in no-tillage and conventional systems. Revista Brasileira de Ciência do Solo 27: 553-561 (in Portuguese, with abstract in English).

Mengel, K.; Kirbky, E.A. 1980. Potassium in crop production. Advances in Agronomy 33: 59-109.

Monterroso, C.; Álvarez, E.; Fernández Marcos, M.L. 1999. Evaluation of Mehlich III reagent as a multielement extractant in mine soils. Land Degradation & Development 10: 35-47.

Mosquera, R.; González, A. 1999. Pasture production in Northern Spain systems. New Zealand Journal of Agricultural Research 42: 125-132.

Papadakis. J. 1966. Climates of the World and their Agricultural Potentialities. J. Papadakis, Buenos Aires, Argentina.

Peech, L.; Alexander, L.T.; Dean, L.A. 1947. Methods of Soil Analysis for Soil-Fertility Investigations, USDA, Washington, DC, USA. (USDA Circular, 757)

Peregrina, F.; Mariscal, I.; Ordonez, R.; González, P.; Terefe, T.; Espejo, R. 2008. Agronomic implications of converter basic slag as a magnesium source on acid soils. Soil Science Society of America Journal 72: 402-411.

Reid, R.L.; Horvath, D.S. 1980. Soil chemistry and mineral problems in farm livestock: a review. Animal Feed Science and Technology 15: 95-167.

Riggs, K.S.; Rimmer, D.L.; Syers, J.K. 1995. Effect of liming on the chemical composition of soils. Journal of the Science of Food and Agriculture 69: 159-167.

Santano, J.; Espejo, R. 1997. Effects of lime and gypsum amendments on cation redistribution and copper, zinc, and manganese availability in a Palexerult from SW Spain. Agrochimica 41: 233-240.

Scott, B.J.; Conyers, M.K.; Fisher, R.; Lill, W. 1992. Particle size determines the efficiency of calcitic limestone in amending acidic soil. Australian Journal of Soil Research 43: 1175-1185.

Stevens, R.J.; Laughlin, R.J. 1996. Effects of lime and nitrogen fertilizer on two sward types over a 10-year period. Journal of Agricultural Science 127: 451-461.

Wendt, J.W. 1995. Evaluation of the Mehlich-3 soil extractant for upland Malawi soils. Communications in Soil Science and Plant Analysis 26: 687-702.

Whitehead, D.C. 1966. Nutrient Minerals in Grassland Herbage: A Review. CABI, Wallingford, UK.

Whitehead, D.C. 1995. Grassland Nitrogen. CABI, Wallingford, UK.

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